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AUTHOR(S):

半田, 岳人

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Summary of thesis: Electron-phonon interactions and thermo-optic properties of metal halide perovskites

Taketo Handa

Metal halide perovskites have attracted much attention as novel photonic device materials. These materials are ternary semiconductors with a general chemical formula ABX_3, where A is a monovalent cation, B is a divalent metal cation, and X is a halogen. The perovskite semiconductors exhibit excellent optoelectronic properties even when they are prepared by a low temperature solution-based process. In particular, solar cells based on lead iodide perovskites have already reached high power conversion efficiencies of over 25%, which is close to the efficiency of high-quality crystalline silicon solar cells. Such high solar cell efficiencies indicate that the lead perovskites are superior materials with few defects within the band gap. In parallel to the efforts devoted to applied research, active research on their fundamental photophysics has been conducted as well. Previous works focused on the precise assessment and control of the band-gap energies of these materials, since the band-gap energy determines the theoretical upper limit of the solar cell efficiency. It has been clarified that the lead iodide perovskites have the band-gap energy well matched with the solar spectrum. Furthermore, it has been shown that by changing the composition of the perovskite material, their band-gap energies can be continuously tuned over a wide wavelength range.

The conversion efficiencies reported so far are still smaller than the thermodynamic upper limit predicted from the band-gap energy (Shockley–Queisser limit). In particular, the spectral shape of the optical absorption near the band edge is important to understand the loss from the limit. A broad absorption tail induces a large drop of the open-circuit voltage, resulting in a significant reduction of the solar cell efficiency. Thus, the so-called Urbach tail, which describes an exponential tail in the optical absorption spectrum below the band gap, determines the effective upper limit of photonic device performance. When no extrinsic effects exist, the steepness of the Urbach tail (defined as the Urbach energy) is determined by the intrinsic electron–phonon interactions in the material. The halide perovskites are polar and ionic semiconductors, where electron–phonon interactions are considered to be strong. Thus, the understanding of the electron–phonon interactions and their impact on the Urbach tail is very important to quantitatively evaluate the actual potential of the perovskites as photonic device materials.

Furthermore, the understanding of the temperature dependences of optical properties of the semiconductor is essential for the efficient operation of photonic devices. The temperature rise induces optical property changes, which can lead to the deterioration of the device performance. For example, in solar cells operating under light illumination, there exist the relaxation of photogenerated carriers via electron–phonon interactions and the nonradiative recombination, which result in an increase in the temperature of the semiconductor layer. Understanding the temperature rise under light illumination and the resulting change of optical properties should be important for implementation of halide perovskites as photonic devices.

In this thesis, we investigated the intrinsic optical properties of metal halide perovskites and clarified their potentials as photonic device materials. Using photoluminescence (PL) spectroscopy, we studied the electron–phonon interactions and the Urbach tail in the tin perovskite $MASnI_3$ (MA= CH_3NH_3) thin films. While the lead perovskite $MAPbI_3$-based solar cells are known to achieve high open-circuit voltages, the lead-free $MASnI_3$-based solar cells usually suffer from a large loss in the open-circuit voltage. It is required to clarify whether the intrinsic optical properties of $MASnI_3$ are suitable for solar cells. The temperature dependence of the PL width of the $MASnI_3$ thin film revealed that the electron–longitudinal optical (LO) phonon interaction dominates the PL broadening near room temperature. Furthermore, the PL spectrum of $MASnI_3$ exhibited a very sharp tail, showing that there is no luminescence signal related to defect states. By using the van Roosbroeck–Shockley relation, we found that $MASnI_3$ has a small Urbach energy of 12 meV at room temperature. This small value is comparable to that observed in the lead perovskite $MAPbI_3$ with superior solar cell properties. From the temperature dependence of the Urbach energy, we concluded that this absorption tail is determined by the intrinsic electron–LO phonon interaction. These results clarified that $MASnI_3$ is actually a promising lead-free solar cell material and has a potential to achieve high open-circuit voltages. Metal halide perovskites have a sharp absorption tail below the band-gap energy, and it was concluded that the strength of the electron–phonon interactions in these perovskites are almost the same as those in conventional polar inorganic semiconductors.

Moreover, the photo-induced lattice temperature rise and the resulting changes in the optical properties were investigated. To precisely evaluate the temperature change of the refractive index under light illumination, optical interferometric measurements were performed on high-quality $MAPbCl_3$ single crystals with negligible surface scattering. We found that light illumination induces a large refractive-index change of $MAPbCl_3$ with a time scale of tens of milliseconds. The result can be well explained by a model based on phonon emission by photogenerated carriers and subsequent thermal conduction. The analysis also clarified that $MAPbCl_3$ has a very low thermal conductivity, resulting in an efficient local heating and the large refractive index change. Through these measurements, we revealed that $MAPbCl_3$ has a large negative thermo-optic coefficient. This negative coefficient is a unique feature since most conventional inorganic semiconductors possess positive thermo-optic coefficients. It was also shown that the negative thermo-optic coefficients in the transparent wavelength region originate from the large thermal expansion coefficient of this material.

We demonstrated that the discovered unique thermo-optic properties enable two new photonic applications. First, we verified that $MAPbCl_3$ can be used to compensate the thermally-induced optical phase shift that occurs in a conventional inorganic semiconductor with a positive thermo-optic coefficient. Additionally, the photo-induced large refractive-index change in $MAPbCl_3$ was utilized to realize an optical phase modulation of visible light. This thesis significantly advances the understanding of intrinsic photophysics in metal halide perovskites and presents new photonic application of the perovskites.